The Crystal Structures of Tritin(II) Bromide Pentafluoride and Ditin(II) Chloride Trifluoride

By **John D. Donaldson, David R. Laughlin,** and **David C. Puxley,** Department of Chemistry, Chelsea College, University of London, Manresa Road, London SW3 6LX

The crystal structures of the title compounds have been determined from *X*-ray photographic data by Patterson and Fourier methods. The crystals of both compounds have pseudo-high-symmetry cells but Sn_3BrF_5 is monoclinic with space group $P2_1/n$ and $Z = 4$ in a unit cell of dimensions $a = 4.27$, $b = 12.70$, $c = 12.70$ Å, $\beta = 90.0°$, and Sn_2ClF_3 is orthorhombic with space group $P2_12_12_1$ and $Z = 4$ in a unit cell of dimensions $a = b = c = 7.88$ Å. Both structures contain infinite tin–fluorine cationic networks in which all the tin atoms have a trigonal pyramidal co-ordination of nearest-neighbour fluorine atoms. The shortest Sn–Br (3.29 Å) and Sn–Cl (3.14 Å) distances are consistent with the presence of free Br^- and Cl^- ions in the lattices.

THE preparations and Mössbauer data of three types of ternary tin(II) halides have been reported[1] *viz.* SnXF, Sn_2XF_3, and Sn_3XF_5. There was no evidence from the Mössbauer spectra to suggest the presence of both Sn–F and Sn–X environments in these compounds. It is possible for the SnXF compounds to have structures similar to that of $SnCl_2$[2,3] but with bridging fluorine atoms as suggested by the Mössbauer data. A structure containing only one Sn environment, and based on that of $SnCl_2$, can also be written[1] for the Sn_2XF_3 compounds but this is not possible for Sn_3XF_5. We have shown[4] in a preliminary study that Sn_3BrF_5 contains an infinite tin(II) fluoride cationic network and free bromide ions. The details of this structure are now reported along with the crystal structure determination for Sn_2ClF_3.

EXPERIMENTAL

The Crystal Structure of Sn_3BrF_5.—Acicular single crystals of tritin(II) bromide pentafluoride were prepared by the literature method.[1] The unit cell, which is pseudo-tetragonal, was determined from rotation and Weissenberg photographs (Cu-K_α radiation) about the needle axis, *a*. Laue photographs for the same mounting, however, showed that the crystal had $2/m$ symmetry and was therefore monoclinic and that it was mounted about a non-unique axis. The intensity data for the crystal were also consistent with monoclinic symmetry.

Crystal Data.—Sn_3BrF_5, $M = 531.0$, Monoclinic, space group $P2_1/n$, $a = 4.27(2)$, $b = 12.70(5)$, $c = 12.70(5)$ Å, $\beta = 90.0(5)°$, $D_c = 5.01$ g cm^{-3}, $Z = 4$, $D_m = 4.79$ g cm^{-3} (by displacement of benzene), $F(000) = 920$, space group $P2_1/n$ from systematic absences, $h0l$ for $h + l = 2n + 1$, and $0k0$ for $k = 2n + 1$. The non-standard space group

---

[1] J. D. Donaldson and B. J. Senior, *J. Chem. Soc.* (*A*), 1969, 2358.

[2] J. M. Van Berg, *Acta Cryst.*, 1961, **14**, 1002.

[3] R. E. Rundle and D. H. Olsen, *Inorg. Chem.*, 1964, **3**, 596.

[4] J. D. Donaldson and D. C. Puxley, *J.C.S. Chem. Comm.*, 1972, 289.

$P2_1/n$ was used since the β-angle of 90° allowed data collection using a crystal mounted about the needle axis, *a*. Photographic multiple-film intensity data (0—5*kl*) were collected on a Nonius integrating Weissenberg camera (equi-inclination setting) using Zr-filtered Mo-K_α radiation. The intensities were measured on a Nonius microdensitometer mkII and then scaled and averaged. Lorentz-polarisation and absorption corrections (for a cylindrical specimen, $\mu\bar{R} = 2.55$) were made, and, after eliminating equivalent reflections, a total of 435 independent reflections above background intensity were obtained. Layer scaling was accomplished by best fit of the observed and calculated data, during the structure refinement. The (100) Patterson projection gave probable positions for the tin and bromine atoms. Refinement of 0*kl* data for the Sn and Br positions, which led to those given in Table 1, gave $R = 0.19$. A 0*kl* Patterson map calculated from the $F(hkl)^2_0$ values gave good peak-position agreement with the projection obtained from the observed data. Interchanging Sn and Br positions increased the value of *R* and led to calculated Patterson projections that gave poorer agreement with the observed map. Approximate *y* and *z* co-ordinates for the fluorine atoms were obtained at this stage from a 0*kl* Fourier synthesis. The *x* co-ordinates for the tin atoms were obtained from a three-dimensional Patterson synthesis by locating the vector peaks between the independent sets of tin atoms. A Fourier synthesis was then used to determine the remaining co-ordinates and the structure was refined to *R* 0.11 by a full-matrix least-squares analysis using unit weights and anisotropic temperature factors. Atomic parameters are given in Table 1 and bond distances in Table 2. The (100) projection [5] of the structure is given in Figure 1.

TABLE 1

Final atomic parameters for Sn_3BrF_5, with estimated standard deviations in parentheses

	x	*y*	*z*	*B*
Sn(1)	0.566 2(15)	0.103 7(4)	0.101 6(4)	*
Sn(2)	−0.079 3(17)	0.160 3(5)	0.370 9(5)	*
Sn(3)	0.128 6(15)	0.377 1(5)	0.154 5(4)	*
Br	0.511 7(24)	0.382 7(9)	0.378 9(8)	*
F(1)	−0.465 9(136)	0.102 4(37)	0.270 6(4)	1.4
F(2)	0.512 6(156)	0.269 9(39)	0.106 4(41)	1.4
F(3)	−0.414 1(126)	0.114 8(45)	0.488 9(38)	1.4
F(4)	0.494 3(167)	0.489 3(40)	0.118 7(44)	1.4
F(5)	−0.004 4(150)	0.139 6(36)	0.151 9(39)	1.4

* Anisotropic temperature factors in the form $\exp(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$

	10^4b_{11}	10^4b_{22}	10^4b_{33}	10^4b_{12}	10^4b_{13}	10^4b_{23}
Sn(1)	71(4)	9(3)	11(4)	83(4)	14(4)	80(4)
Sn(2)	157(5)	15(4)	14(4)	127(4)	24(4)	120(4)
Sn(3)	78(4)	13(4)	12(4)	96(4)	17(4)	88(4)
Br	210(6)	26(6)	27(6)	239(6)	50(6)	251(6)

TABLE 2

Bond distances (Å) and angles (°) for Sn_3BrF_5, with estimated standard deviations in parentheses

Sn(1)–F(1)	2.15(5)	Sn(2)–F(1)	2.21(6)
Sn(1)–F(2)	2.12(5)	Sn(2)–F(3)	2.15(5)
Sn(1)–F(5)	1.99(6)	Sn(2)–F(4)	2.21(5)
Sn(3)–F(2)	2.21(6)	Sn(1)–Br	3.35(3)
Sn(3)–F(3)	2.11(5)	Sn(2)–Br	3.32(2)
Sn(3)–F(4)	2.16(6)	Sn(3)–Br	3.29(3)

F(1)–Sn(1)–F(2)	88.4(1.8)
F(1)–Sn(1)–F(5)	75.0(2.2)
F(2)–Sn(1)–F(5)	82.2(2.2)
F(1)–Sn(2)–F(3)	79.4(2.0)
F(1)–Sn(2)–F(4)	80.2(2.2)
F(3)–Sn(2)–F(4)	78.6(2.1)
F(2)–Sn(3)–F(3)	79.6(2.1)
F(2)–Sn(3)–F(4)	79.2(1.9)
F(3)–Sn(3)–F(4)	79.7(2.2)

The Crystal Structure of Sn_2ClF_3.—Single crystals of ditin(II) chloride trifluoride were prepared by the literature method.[1] The unit cell which is pseudo-cubic was determined from precession, rotation, and Weissenberg photographs about the *a*-axis and one of the 11.14 Å axes, which form face diagonals of the smaller pseudo-cubic unit cell. Laue photographs with the latter mounting showed the symmetry to be lower than the cubic space group, $P2_13$, used by Bergerhoff and Goost.[6] Intensity data for the crystal mounted along the *a*-axis were consistent with orthorhombic symmetry.

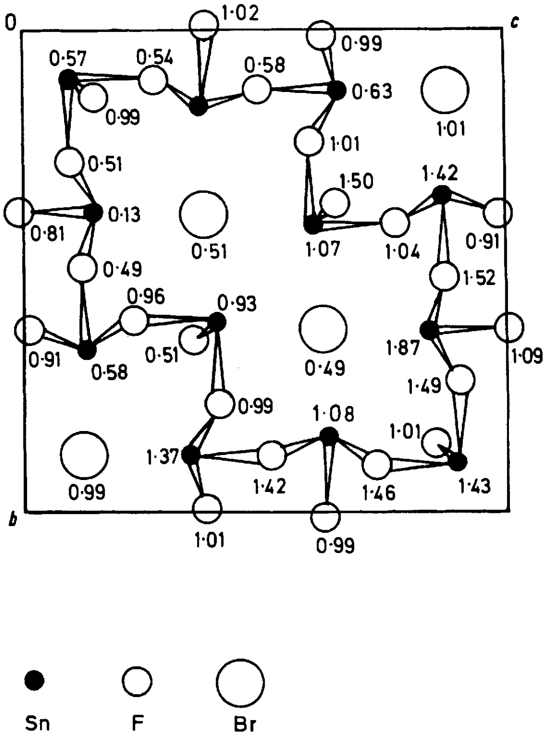

FIGURE 1 (100) Projection of the unit cell of Sn_3BrF_5. Figures represent the positions of the atoms along the *x*-direction

Crystal Data.—Sn_2ClF_3, $M = 329.9$, Orthorhombic, $a = b = c = 7.880(5)$ Å, $U = 489.3$ Å^3, $D_c = 4.48$ g cm^{-3}, $Z = 4$, $D_m = 4.19$ g cm^{-3} (by displacement of benzene), $F(000) = 576$, space group $P2_12_12_1$. Photographic multi-film intensity data (*h*0*l*—*h*10*l*) were collected, by the same method used for Sn_3BrF_5, about the 11.14 Å axis and transformed to those for the smaller pseudo-cubic cell. Lorentz-polarisation corrections were made but absorption was neglected ($\mu = 26.7$ for Mo-K_α radiation gives an optimum crystal thickness of 0.19 mm, maximum crystal thickness 0.19 mm). After eliminating equivalent reflections, 744 independent reflections above background intensity were obtained.

The tin positions were found from a three-dimensional Patterson synthesis. Atomic parameters, isotropic *B*-factors and scale factors were refined in a full-matrix least-

---

[5] D. C. Puxley, Ph.D. Thesis, University of London, 1972.

[6] G. Bergerhoff and L. Goost, *Acta Cryst.*, 1974, **B30**, 1362.

squares analysis, to give R 0.13. A quarter-cell Fourier map was calculated using the tin positions, allowing the chlorine atoms to be found. Inclusion of the Cl in a further refinement gave R 0.10. The fluorine positions were determined from a difference-Fourier map. Four bad reflections for which $|F_o| < 2|F_c|$ or $|F_c| < 2|F_o|$ were removed. The remaining 740 reflections were used to refine all atomic positions, with anisotropic temperature factors for Sn when convergence occurred at R 0.056. Atomic parameters are given in Table 3 and bond distances and angles in Table 4. The (001) projection of the structure is in Figure 2. The observed and calculated structure factors are in Supplementary Publication No. SUP 21923 (12 pp., 1 microfiche).*

TABLE 3

Final atomic parameters for Sn_2ClF_3 with estimated standard deviations in parentheses

	x	y	z	$B(\text{Å}^2)$
Sn(1)	−0.067 2(2)	−0.067 7(2)	−0.067 3(2)	*
Sn(2)	−0.399 1(2)	−0.398 9(2)	−0.399 1(2)	*
Cl	0.262 6(7)	0.259 6(8)	0.261 0(7)	2.38(1)
F(1)	−0.124 7(16)	0.132 6(15)	0.114 6(15)	1.86(1)
F(2)	0.116 2(17)	−0.123 7(16)	0.134 4(14)	2.06(1)
F(3)	0.133 1(16)	0.118 6(16)	−0.124 0(15)	2.04(1)

* Anisotropic temperature factors, of the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$

	10^4b_{11}	10^4b_{22}	10^4b_{33}	10^4b_{12}	10^3b_{13}	10^4b_{23}
Sn(1)	74(2)	75(2)	81(2)	−54(2)	−78(2)	−9(2)
Sn(2)	81(3)	83(3)	86(2)	86(2)	13(2)	13(2)

TABLE 4

Bond angles (°) and bond distances (Å) for Sn_2ClF_3 with estimated standard deviations in parentheses

Sn–Sn distances			
Sn(1)–Sn(2)	3.917(6)		
Sn(1)–Sn(1)	4.990(8)		
Sn(2)–Sn(2)	4.856(8)		
Tin co-ordination			
Sn(1)–F(1)	2.180(4)	Sn(1)–F(2)	2.193(4)
Sn(1)–F(3)	2.202(4)		
Next nearest F	3.506(6)		
Nearest Cl	3.143(15)		
Sn(2)–F(1)	2.110(4)	Sn(2)–F(2)	2.097(4)
Sn(2)–F(3)	2.108(4)		
Next nearest F	3.379(6)		
Nearest Cl	3.294(14)		
F–Sn–F bond angles			
F(1)–Sn(1)–F(2)	78.8(7)	F(1)–Sn(1)–F(3)	78.5(7)
F(2)–Sn(1)–F(3)	80.0(7)	F(1)–Sn(2)–F(2)	81.9(8)
F(1)–Sn(2)–F(3)	80.9(7)	F(2)–Sn(2)–F(3)	81.4(8)

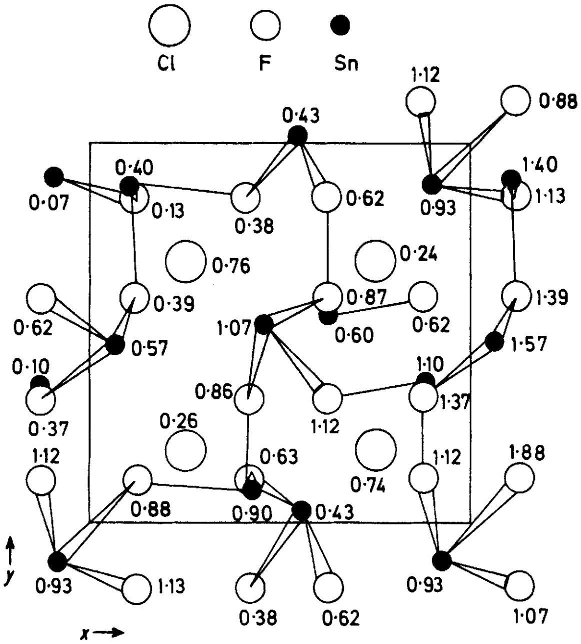

FIGURE 2 (001) Projection of the unit cell of Sn_2ClF_3. Figures represent the positions of the atoms along the z-direction

DISCUSSION

The structure of Sn_3BrF_5 consists of an infinite two-dimensional fluorine-bridged network. Each tin is in pyramidal three-co-ordination. Two of the tin atoms [Sn(2) and Sn(3)] are in almost identical environments, being bonded to three bridging fluorine atoms. The third tin [Sn(1)] is bonded to two bridging [F(1) and F(2)] and one non-bridging [F(5)] fluorine atoms. The bromine atoms are at a distance of 3.3 Å from the nearest tin and must therefore be considered to be free anions and not bonded to tin (*cf.* Sn–Br = 2.55 Å for $SnBr_2$ in the gas phase [7]). The compound is therefore more correctly formulated as $(Sn_3F_5)_n{}^{n+}(Br^-)_n$. The bond distances and angles for Sn_3BrF_5 are compared with those in other structures in Table 5.

TABLE 5

Bond distances (Å) and angles (°) in tin–fluorine compounds

		Distances	Angles
$KSnF_3\cdot\frac{1}{2}H_2O$		2.27, 2.27, 2.04, 2.01	89.7
$NaSn_2F_5$		2.22, 2.13, 1.99	81.2, 84.1, 89.3
Sn_3BrF_5	Sn(1)	2.15, 2.13, 1.99	88.4, 75.0, 81.7
	Sn(2)	2.21, 2.15, 2.20	79.4, 80.2, 78.7
	Sn(3)	2.21, 2.11, 2.16	79.5, 79.2, 79.8
Sn_2ClF_3	Sn(1)	2.20, 2.19, 2.18	80.0, 78.8, 78.5
	Sn(2)	2.11, 2.10, 2.11	81.9, 81.4, 80.9

Sn_2ClF_3 consists of an infinite three-dimensional cationic network $(Sn_2F_3)_n{}^{n+}$ with chlorine atoms occupying holes in the structure. This structure is therefore similar to that of Sn_3BrF_5, except that all the fluorine atoms in Sn_2ClF_3 are bridging, giving rise to a three-dimensional cationic network instead of a two-dimensional one. The material is more correctly formulated as $(Sn_2F_3)_n{}^{n+}(Cl^-)_n$ because the Sn–Cl distances [7] of 3.14 Å are too long for bonding contacts. The structure contains two similar tin atoms, both with a pyramidal three-co-ordinate environment (Table 4). Sn(2) has bond distances in the range 2.10—2.11 Å with F–Sn–F bond angles from 78.5 to 80.0° and Sn(1) has bond distances of 2.18—2.20 Å with F–Sn–F bond angles of 80.9—81.9°. Both tin atoms are therefore in a virtually undistorted trigonal-pyramidal co-ordination, with much less distortion than the tin atoms in

---

* For details, see Notices to Authors, No. 7, in *J.C.S. Dalton*, 1976, Index issue.

[7] M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, 1941, **37**, 406.

$NaSn_2F_5$,[8] but with very similar environments to Sn(2) and Sn(3) in Sn_3BrF_5. The environments of the tin atoms in both structures are typical of those found generally in Sn^{II} materials, *i.e.* with trigonal-pyramidal sites. A regular square-pyramidal environment is known for SnO,[9] but this is probably a result of Sn–Sn interactions along the relatively short metal–metal distance. Most compounds of Sn containing four-co-ordinate metal have distorted square-pyramidal environments consisting of two bonds shorter than those found in three-co-ordinate structures and two longer. This effect is seen by comparing bond lengths in Sn_2ClF_3 and Sn_3BrF_5 with those of $KSnF_3\cdot\frac{1}{2}H_2O$ [10] (Table 5). The structure of Sn_4OF_6,[11] originally thought to be an orthorhombic form of SnF_2,[12] probably also contains four-co-ordinate tin atoms, three tins with bonds to one oxygen and three fluorines and a fourth tin with four fluorine atoms in co-ordination. The final refinement of this structure has, however, not yet been completed.

The Mössbauer data for Sn_2ClF_3 and Sn_3BrF_5 obtained previously[1] suggested that Sn–F and Sn–Cl(Br) bonds could not both be present. This is confirmed by the crystal structures. Both compounds give quadrupole-split resonance lines with shifts typical of those found for materials with Sn–F environments. Although the crystal structures for each shows that the tin atoms within the cells are not identical, they are sufficiently similar to give overlapping Mössbauer resonance lines which cannot be resolved into those from individual sites.

The observed pseudo-tetragonal symmetry of the Sn_3BrF_5 structure is explained by the close-approximation to *mm* symmetry of the 100 projection (Figure 1). For Sn_2ClF_3 the pseudo-cubic symmetry arises because the heavier Sn and Cl atoms are in approximately cubic cell positions (Table 3). The positions of the F atoms, however, eliminate the possibility of a cubic lattice for Sn_2ClF_5. Other pseudo-high-symmetry structures involving infinite three-dimensional structures are known, *e.g.* the mineral boracite, $Mg_3ClB_7O_{13}$, has a pseudo-cubic low-temperature form [13] and a cubic high-temperature modification consisting of an infinite three-dimensional array of B_5O_{12} units.

Polynuclear cations are well established [14,15] in the basic salt chemistry of tin(II) and the crystal structure of $Sn_3O(OH)_2SO_4$, for example, is known [15] to contain the $[Sn_3O(OH)_2]^{2+}$ cation. Similar species are known in the basic salt chemistry of other ns^2 ions such as Pb^{2+} and Bi^{3+}.[14] The crystal structures described here are, however, the first examples of the formation of polymeric Sn^{II}–F network cations.

[6/1334 *Received, 8th July, 1976*]

---

[8] R. R. McDonald, A. C. Larsen, and D. T. Cromer, *Acta Cryst.*, 1964, **17**, 1104.

[9] W. J. Moorse and L. Pauling, *J. Amer. Chem. Soc.*, 1941, **63**, 1392.

[10] G. Bergerhoff, L. Goost, and E. Schultz-Rhonhof, *Acta Cryst.*, 1968, **B24**, 803.

[11] J. D. Donaldson and J. T. Southern, unpublished work.

[12] J. D. Donaldson, R. Oteng, and B. J. Senior, *Chem. Comm.*, 1965, 618.

[13] R. W. G. Wyckoff, ' Crystal Structures,' Interscience, New York, 1964, vol. 2.

[14] J. D. Donaldson, *Progr. Inorg. Chem.*, 1967, **8**, 287.

[15] C. G. Davis, J. D. Donaldson, and D. R. Laughlin, *J.C.S. Dalton*, 1975, 2241.